Missouri Department of Natural Resources

Biological Assessment and Metals Characterization Report

Silver Creek (WBID 3244)
Newton County, Missouri

Fall 2012 – Spring 2013

Prepared for:
Missouri Department of Natural Resources
Division of Environmental Quality
Water Protection Program
Water Pollution Control Branch

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1.0 Introduction

Silver Creek (Water Body Identification [**WBID]** 3244) is a small stream located in northern Newton County, Missouri, in the Ozark/Neosho Ecological Drainage Unit (**EDU,** Table 1, Figure 1). The 6.2 square-mile Silver Creek watershed includes urban uses such as commercial, residential, and Interstate 44 in southern Joplin, Missouri. The stream is approximately 1.9 miles long from its headwaters to its confluence with Shoal Creek.

Silver Creek is a class P stream with designated beneficial uses for livestock and wildlife watering (**LWW**), protection of warm water aquatic life (**AQL**), and whole body contact (**WBC**), category B (MDNR 2014). The WBC "Category B" applies to waters designated for whole body contact recreation not contained within category A. Category A is defined as:

> *Waters that have been established by the property owner as public swimming areas welcoming access by the public for swimming purposes and waters with documented existing whole body contact recreational use(s) by the public. Examples of this category include, but are not limited to: public swimming beaches and property where whole-body contact recreational activity is open to and accessible by the public through law or written permission of the landowner (MDNR 2014).*

1.1 Justification

Much of northern Newton and southern Jasper counties, including the Joplin area, have been extensively mined for lead in the past. Presently, the Silver Creek upper watershed lies within urban Joplin, which includes commercial and interstate highway properties. The lower watershed comprises residential and commercial properties. These potential sources may influence the ability of Silver Creek to support the "protection of warm water AQL" designated beneficial use. A stream habitat assessment, biological assessment (which includes benthic macroinvertebrate community and water quality analyses), surface water and pore water dissolved metals analyses, and total metals characterization of fine sediment are included in this study of Silver Creek.

This study was requested by the Missouri Department of Natural Resources (**MDNR**), Water Protection Program (**WPP**), Water Pollution Control Branch (**WPCB**). The Silver Creek 2012 – 2013 biological assessment and heavy metals characterization study were conducted by the Division of Environmental Quality (**DEQ**), Environmental Services Program (**ESP**), Water Quality Monitoring Section (**WQMS**) and Chemical Analysis Section (**CAS**).

1.2 Objectives

- Assess the quality of stream habitat.
- Assess the "protection of warm water AQL" designated beneficial use status using the benthic macroinvertebrate community.
- Assess physicochemical water quality.
- Determine surface water dissolved metals concentrations.
- Determine pore water dissolved metals concentrations.
- Describe the heavy metals character of the fine sediment.

1.3 Null Hypotheses

1) Stream habitat quality at Silver Creek #1 will be comparable to the stream habitat controls.
2) Macroinvertebrate Stream Condition Index (**MSCI**) scores will indicate that Silver Creek is fully supporting of the AQL and individual biological metrics will be within the optimum scoring range of wadeable/perennial reference stream biological criteria during the fall and spring seasons.
3) Stream size will not be a factor in determining the support category and the dominant macroinvertebrate community assemblage will be similar to reference streams.
4) Physicochemical water quality variables will be within acceptable parameters as specified in Missouri's Water Quality Standards (**WQS**, MDNR 2014).
5) The dissolved metals in the surface water and the pore water of the substrate will be within acceptable hardness-dependent parameters outlined in Missouri's WQSs.
6) The heavy metals character (i.e., cadmium, lead, zinc) in the substrate fine sediment will be below threshold levels in Silver Creek.

2.0 Methods

Kenneth B. Lister, Carl Wakefield, and ESP personnel conducted this study. Methods and study timing are outlined in this section. The study area and station descriptions, EDUs, and land uses are identified. Stream habitat assessment procedures are discussed. Biological assessment procedures, which include macroinvertebrate community and physicochemical water collection methods and analyses, are discussed in this section. Pore water metals collection using peepers and analyses conducted are discussed in this section. Methods for fine sediment heavy metals characterization are outlined in this section.

2.1 Study Timing

Sampling was conducted at Silver Creek in the fall of 2012 and the spring of 2013. The stream habitat was assessed on September 6, 2012. Stream macroinvertebrate, water quality, and surface water dissolved metals samples were collected on October 4, 2012, and April 2, 2013. Pore water samplers (peepers) were deployed for collection of dissolved metals from August 1 to August 14, 2013. Fine sediment was collected on September 6, 2012, and April 2, 2013.

2.2 Study Area, Station Locations, and Descriptions

Silver Creek and all streams included in this study are located in the Ozark/Neosho EDU (Table 1, Figure 1). One station was allocated for the Silver Creek 2012 – 2013 project (Table 1, Figure 2). One stream habitat assessment control stream was used in this project.

2.2.1 Ecological Drainage Unit

As mentioned, Silver Creek, the references, candidate reference, and control streams are located within the Ozark/Neosho EDU (Figure 1). EDUs are areas that are delineated and identified by their natural terrestrial physiographic division and major riverine watershed component. EDUs are further described in Sowa et al. (2007). Streams of similar size within an EDU are expected to contain similar habitat conditions and aquatic communities. Comparisons of habitat,

biological, and physicochemical results between test streams and references or similar-size control streams within the same EDU should then be appropriate.

Table 1
Locations and Descriptions of Silver Creek and Mikes Creek Stations

Station	County	Location	Description; WBID	Purpose; Class
Silver Creek #1	Newton	SE¼ sec. 26, T. 27 N., R. 33 W. E366137 N4099039	Joplin South Middle School; 3244	Test; P
Mikes Creek #3	McDonald	NW¼ sec. 29, T. 23 N., R. 29W. E402214 N4060351	Upstream Highway U; N/A	SHAPP Control; U

P=Permanent; U=Unclassified

2.2.2 Land Use Description

Using a 12-digit Hydrological Unit scale (**HUC-12**), the Silver Creek watershed land use was compared to Mikes Creek (the habitat assessment control site) and land use in the Ozark/Neosho EDU overall (Table 2). Percent land use (cover) data were derived from Thematic Mapper satellite data collected between 2000 and 2004 and interpreted by the Missouri Resource Assessment Partnership (**MoRAP**).

Land use (or cover) should be considered when examining stream habitat assessment or biological assessment results between stations or within the EDU. Land cover was relatively similar among the Silver Creek and control stations, as well as the overall Ozark/Neosho EDU. Grassland and forest were the dominant two land uses at Silver Creek, Mikes Creek, and the EDU. The major difference between Silver Creek and Mikes Creek or the EDU was urban land use. Silver Creek had approximately 12 percent urban land use, as opposed to <1 and 4 percent at Mikes Creek and the EDU, respectively. Urban land use may be a potential contributor to the support of beneficial uses at Silver Creek.

Table 2
Percent Land Use by HUC-12 in Silver Creek, Mikes Creek,
and the Ozark/Neosho EDU

Stations	HUC-12	Urban	Crops	Grass	Forest	Wetland	Open-water
Silver Creek	110702070805	11.7	1.7	41.9	42.8	1.4	0.7
Mikes Creek (2009)	110702080105	0.9	1.9	32.2	65.0	0.0	0.0
Ozark/Neosho EDU	--	4.0	15.0	52.0	25.0	1.0	0.0

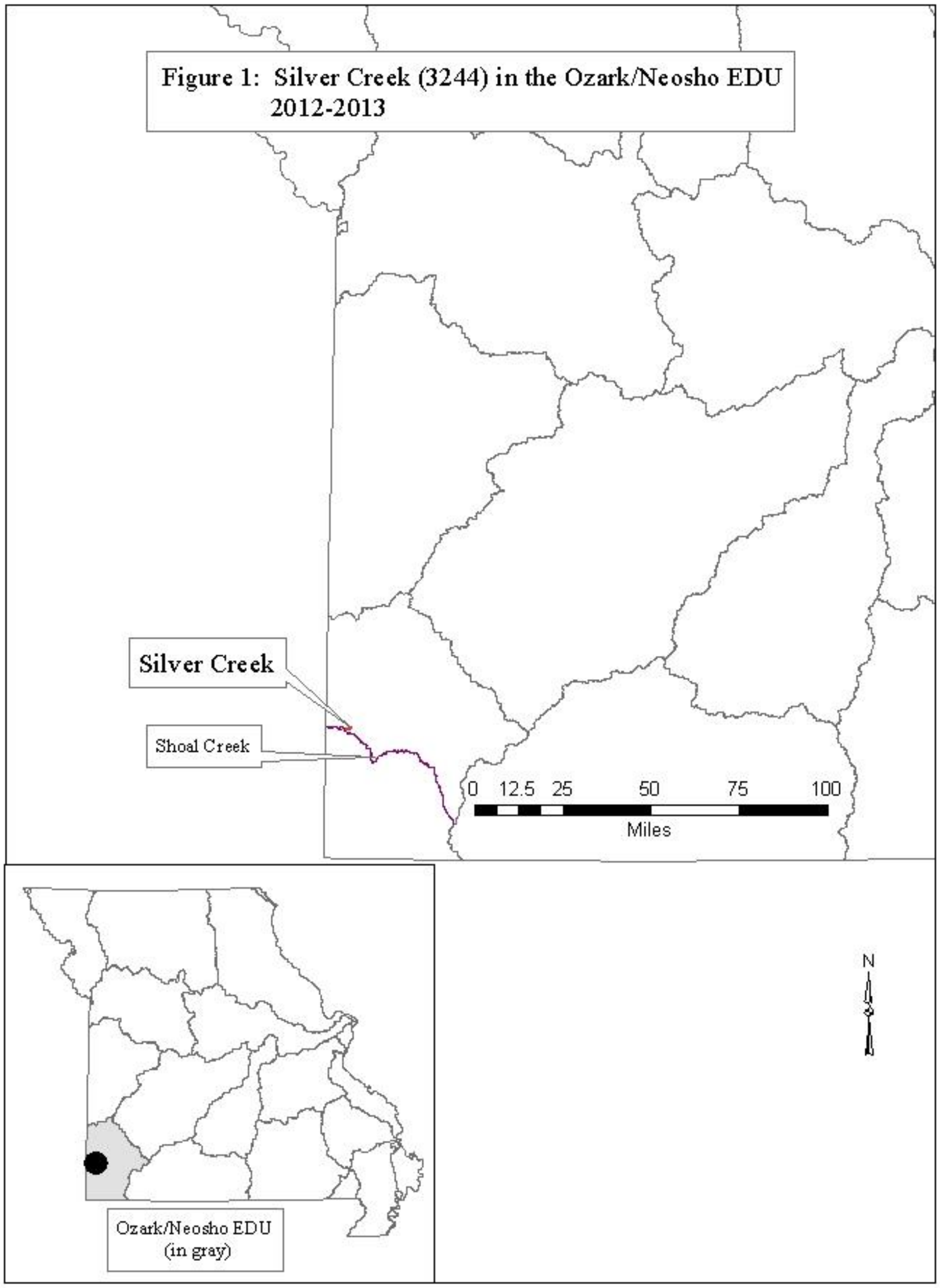


Figure 1: Silver Creek (3244) in the Ozark/Neosho EDU
2012-2013
Silver Creek
Shoal Creek
0 12.5 25 50 75 100
Miles
N
Ozark/Neosho EDU
(in gray)

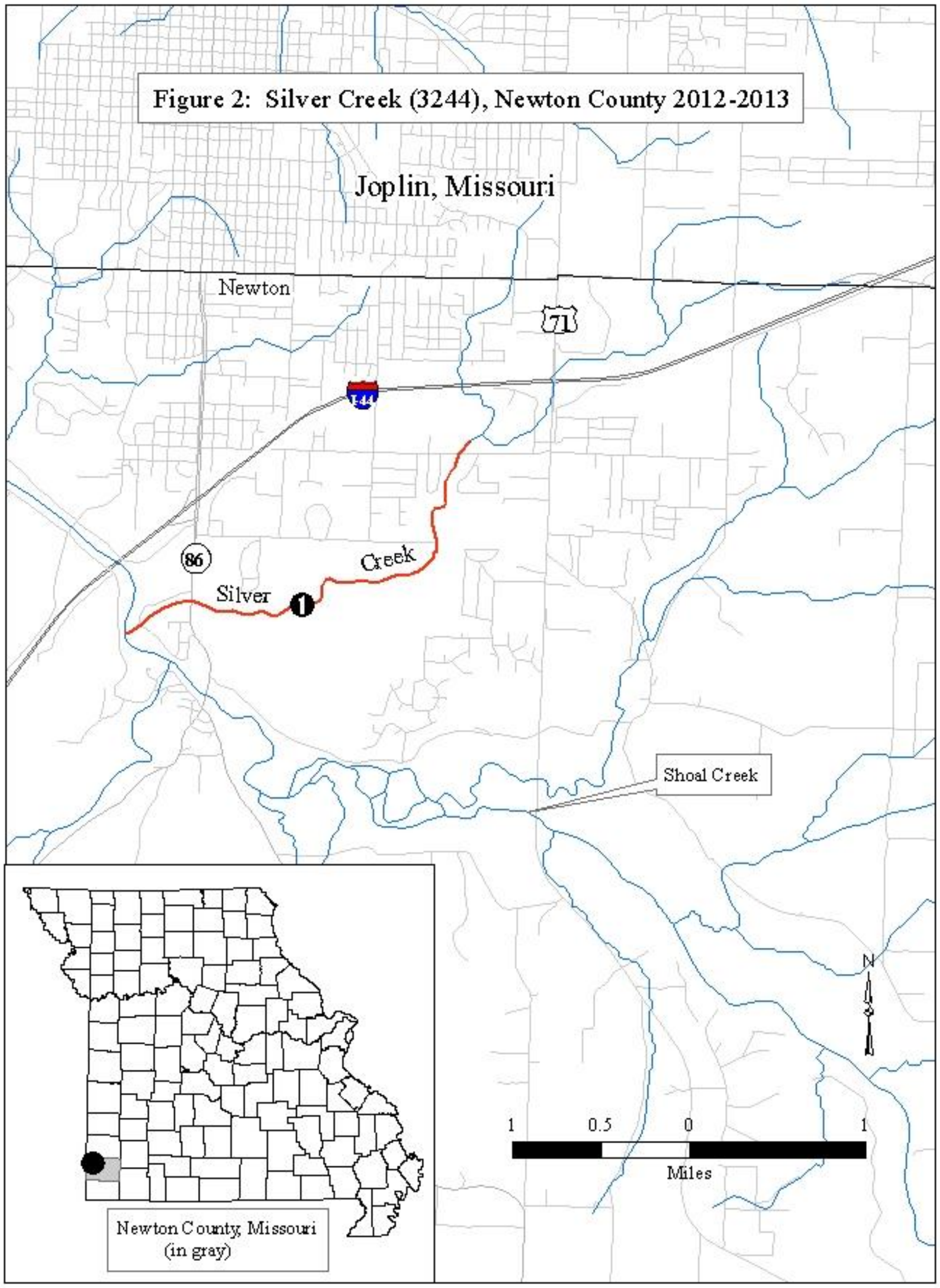


Figure 2: Silver Creek (3244), Newton County 2012-2013
Joplin, Missouri
Newton
71
I-44
86
Silver
Creek
1
Shoal Creek
N
1
0.5
0
1
Miles
Newton County, Missouri
(in gray)

2.3 Stream Habitat Assessment Project Procedure

The standardized *Stream Habitat Assessment Project Procedure* (**SHAPP**) was followed as described for riffle/pool prevalent streams (MDNR 2010a). According to the SHAPP, the quality of an aquatic community is based on the ability of the stream to support the aquatic community. If SHAPP scores at test stations are ≥75% of the mean control scores, the stream habitat at the test station is considered to be comparable to the control stream. Two SHAPPs from Mikes Creek #3 were used as controls; one was recorded in 2009 and another was recorded in 2013. The SHAPP score from Silver Creek was compared to the mean score from Mikes Creek and the Silver Creek score was expressed as a percentage of the mean control.

2.4 Biological Assessment

Sampling was conducted as described in the MDNR *Semi-quantitative Macroinvertebrate Stream Bioassessment Project Procedure* (**SMSBPP,** MDNR 2012). Biological assessments consist of macroinvertebrate community and physicochemical water sampling and analyses. Primary and secondary metrics were examined and are grouped by season and station.

2.4.1 Macroinvertebrate Sampling, Identification, and Analyses: Primary Metrics

Macroinvertebrate samples were collected from multiple habitats, as described in the SMSBPP (MDNR 2012). Silver Creek is considered a riffle/pool dominant stream. As such, coarse substrate (**CS,** riffle), non-flowing (**NF**) water over depositional substrate, and rootmat (**RM**) habitats were sampled. Macroinvertebrates were subsampled in the WQMS lab according to the SMSBPP (MDNR 2012) and identified to specific taxonomic levels that allowed for standardized calculation of the metrics (MDNR 2010b).

Primary analyses of the macroinvertebrate community consisted of examination of Silver Creek's MSCI scores and the individual metric scores that were used to generate the MSCI scores (MDNR 2012).

An MSCI is a qualitative rank measurement of a stream's aquatic biological integrity (Rabeni et al.1997). The MSCI was further refined to include generation of biological criteria using data from wadeable/perennial reference streams (**BIOREF**) for each EDU, as described in *Biological Criteria for Perennial/Wadeable Streams* (MDNR 2002). A station's MSCI score ultimately assesses the ability of the stream to support the designated beneficial use for the protection of warm water AQL.

An MSCI score is a compilation of rank scores (i.e., metric scores) that are assigned to individual biological metrics as measures of biological integrity compared to BIOREFs. Four primary biological metrics are used to calculate the MSCI per station: 1) Taxa Richness (**TR**); 2) Ephemeroptera/Plecoptera/Trichoptera Taxa (**EPTT**); 3) Biotic Index (**BI**); and 4) Shannon Diversity Index (**SDI**). Each metric value was compared to its corresponding BIOREF scoring range in Tables 4a and 5a; metric scores (5, 3, 1) were assigned to each individual metric. The four metric scores were compiled to create the MSCI for each station. The MSCI scores determined the "support of beneficial use" category based on the following ranges: 20-16 = full support; 14-10 = partial support; and 8-4 = non-support of the AQL beneficial use designation. MSCI scores were examined by station and grouped by season (Tables 4a and 5a).

Individual biological metric scores were evaluated to determine their relative contribution to the MSCI and generally identify the makeup of the macroinvertebrate community. Variations in certain metric scores may also aid in identifying sources of impairment.

Silver Creek is smaller than most BIOREF streams in the Ozark/Neosho EDU that were used to develop the MSCI. It has not yet been determined if, or how much, stream size contributes to the quality of a stream's macroinvertebrate community. Consequently, the potential exists for the biological support category to be affected by stream size or variables associated with size. In order to determine if stream size had an effect on the MSCI and the support category, individual metric values were compared to criteria that were generated using similar-size candidate reference stream data. Small candidate reference stream criteria used here are from the *Biological Assessment Report for Beef Branch and Jacobs Branch 2010-2011* (MDNR 2011a). Small candidate reference stream MSCI scores were developed in the same manner as the original MSCI (Tables 4b and 5b). A change in the MSCI (**ΔMSCI**) should indicate that stream size may have had an effect on the MSCI score, while a change in the support category indicated that the change was substantial (**ΔSupport**).

2.4.2 Macroinvertebrate Analysis: Dominant Macroinvertebrate Taxa

Secondary metrics are used to identify specific details about the macroinvertebrate community composition that may highlight trends and support findings of the primary metrics. The secondary metric used in this study was the dominant macroinvertebrate taxa (**DMT**) metric.

The DMT assemblage was examined for Silver Creek as described in the SMSBPP (MDNR 2012). The 10 most abundant (i.e., dominant) taxa from the Ozark/Neosho EDU BIOREF streams (in aggregate) were compared to their respective abundance in the test stream. These comparisons may identify similarities between BIOREF and test stream macroinvertebrate communities in higher quality streams; dissimilarities may help identify the type and source of pollutants in impaired streams. The DMT metrics were examined by season.

A complete taxa list is available in the attached Macroinvertebrate Database Bench Sheets Report (Appendix A).

2.4.3 Physicochemical Water Sampling and Analyses

Physicochemical water samples were handled according to the applicable MDNR, ESP Standard Operating Procedures (**SOPs**) for sampling and analyzing physicochemical water samples. Results for physicochemical water variables are arranged by season and station.

Physicochemical water parameters consisted of field measurements and grab samples. Water was sampled according to the SOP MDNR-ESP-001 *Required/Recommended Containers, Volumes, Preservatives, Holding Times, and Special Sampling Considerations* (MDNR 2011b). Temperature (°C), pH, conductivity (µS/cm), dissolved oxygen (mg/L), and discharge (cubic feet per second [**cfs**]) were measured *in situ*. The ESP's CAS in Jefferson City, Missouri, conducted analyses for ammonia as nitrogen (**NH_3-N**; mg/L), nitrate+nitrite as nitrogen (**NO_3+NO_2-N**; mg/L), total nitrogen (**TN**; mg/L), chloride (**Cl**; mg/L), sulfate (**SO_4**; mg/L), total phosphorus (**TP**; mg/L), and non-filterable residue (**NFR**; mg/L). Turbidity (nephelometric turbidity unit,

NTU) was measured and recorded in the WQMS biology laboratory. All samples that were transported to ESP were kept on ice.

Test station physicochemical water parameters were compared to Missouri's WQS (MDNR 2014). Interpretation of acceptable limits within the WQS may be dependent on a stream's classification and its beneficial use designation. Furthermore, acceptable limits for parameters may be dependent on the rate of exposure. These exposure or toxicity limits are based on the lethality of a toxicant given long-term (chronic toxicity) or short-term exposure (acute toxicity).

2.4.4 Discharge

Stream discharge was measured using a Marsh-McBirney Flowmate 2000™ flow meter at each station. Velocity and depth measurements were recorded at each station according to SOP MDNR-ESP-113 *Flow Measurement in Open Channels* (MDNR 2013).

2.5 Dissolved Metals

The CAS analyzed dissolved metals concentrations in surface water and pore water samples from Silver Creek. Surface water was collected as a grab sample during each visit. Substrate pore water was collected using peepers in a 14-day period during August 2013.

2.5.1 Surface Water Metals

Surface water samples were collected and analyzed for dissolved metals during the fall and spring sample seasons. Water samples used for dissolved metals analysis were filtered using a 0.45µm filter and preserved as outlined in MDNR-ESP-001 (MDNR 2011b). Chemical analyses were conducted to determine the concentrations of the following dissolved metals: barium, (**Ba**); cadmium, (**Cd**); calcium, (**Ca**); cobalt, (**Co**); copper, (**Cu**); lead, (**Pb**); magnesium, (**Mg**); nickel, (**Ni**); and zinc, **(Zn**). Hardness as $CaCO_3$ values were calculated using Ca and Mg according to Standard Methods (2340 B, 2011) and used to identify chronic and acute metals toxicity concentrations listed in Missouri's WQS (MDNR 2014).

2.5.2 Pore Water Metals

Passive sampling devices (peepers, Serbst et al. 2003, Brumbaugh et al. 2007) were used *in situ* to collect substrate pore water samples for dissolved metals analysis. Materials used to construct the peepers were donated by the United States Geological Survey **(USGS)**, Columbia Environmental Research Center (**CERC**) in Columbia, Missouri. Peepers were prepared as described in Brumbaugh et al. (2007) and deployed in Silver Creek from August 1 to August 14, 2013. Three peepers were buried in the substrate to a depth of approximately two inches in areas near the heads of riffles CS as described by Brumbaugh et al. (2007) and three were placed approximately two inches deep in pools NF. One peeper that was placed in a pool could not be found at the end of the deployment period. Pore water samples were analyzed for dissolved metals: barium, cadmium, calcium, cobalt, copper, iron (**Fe**), lead, magnesium, manganese (**Mn**), nickel, and zinc. Hardness as $CaCO_3$ was calculated using calcium and magnesium concentrations according to Standard Methods (2340 B, 2011). Results were compared to Missouri WQS (MDNR 2014).

If heavy metals concentrations were elevated in the pore water, pore water toxicity units **(PWTU)** were developed (United States Environmental Protection Agency **[USEPA]** 2005, Besser et al.2009a, 2009b, MacDonald et al. 2009, Allert et al. 2008, 2011) and compared to threshold levels developed by MacDonald et al. (2009). A PWTU is the pore water dissolved metal concentration divided by the hardness dependent chronic level water quality standard. Chronic metals concentrations are listed in the Missouri WQS (MDNR 2014). A PWTU under 1.0 can be expected to be non-toxic (USEPA 2005, Besser et al. 2009b). The PWTUs may be summed (∑**PWTU**, Besser et al. 2009a) to examine potential toxicity from metals mixtures and may be compared to pore water toxicity thresholds (MacDonald et al. 2009). The ∑PWTU threshold value for divalent metals, which includes cadmium, lead, and zinc, is 1.03. A sample above this threshold is expected to be toxic to benthic organisms.

Two types of peeper blanks were used for quality control. Field blanks were prepared to identify deployment and retrieval influences. The field blanks were sealed in a container, filled with ultrapure deoxygenated and deionized water, and placed in a cooler with ice for deployment and retrieval, as described by Brumbaugh et al. (2007). During the deployment period, the container with peepers was placed in a refrigerator that maintained a constant temperature near 3°C. The field blank and test peepers were capped in the field at the conclusion of the sample period. All sample bottles were placed in separate plastic bags, placed on ice, and transported to CERC. At CERC, the samples were removed and the containers were rinsed with 1% HNO_3 into a 100 mL Nalgene® bottle. Each sample was diluted with the 1% HNO_3 to achieve a 1:1 ratio. A bottle blank was prepared using 100 mL of 1% HNO_3 to evaluate potential effects from peeper components. The pore water samples were analyzed for dissolved metals by the CAS. Results were multiplied by two to account for dilution.

2.6 Fine Sediment Character

Instream deposits of benthic fine sediment (i.e., particle size ca. <2 mm) were collected and characterized for total recoverable cadmium, lead, and zinc (mg/kg). The CAS conducted metals character analyses.

Fine sediment was collected from Silver Creek #1 to be characterized for metals concentrations. Three samples were individually collected in a two-ounce glass jar and composited into one eight-ounce glass jar per station. Individual concentrations and mixture of metals thresholds were compared to thresholds levels (mg/kg).

Individual metals concentrations were compared to Probable Effects Concentrations (**PEC**s, MacDonald et al. 2000). A PEC is the threshold level for a contaminant above which harmful effects are likely to be observed. MacDonald et al. (2000) found PECs to be reliable for 10 metals (including cadmium, lead, and zinc) in classifying sediments as nontoxic or toxic. The PEC for lead is 128 mg/kg dry weight, the PEC for cadmium is 4.98 mg/kg, and the PEC for zinc is 459 mg/kg (MacDonald et al. 2000). Individual metals were further examined using Probable Effects Concentration Quotients ([**PEQ**]; MacDonald et al. 2000, 2009, Ingersoll et al. 2001, 2002, 2009, Besser et al. 2008, 2009a). The PEQ is the total recoverable concentration divided by that metal's respective PEC (MacDonald et al. 2000). A PEQ greater than 1.0 may be associated with an increased risk of toxicity (Besser et al. 2009a).

The effects from a mixture or combination of cadmium, lead, and zinc may be accounted for by developing the sum of PEQ (∑**PEQ**) or a mean PEQ. The ∑PEQ (Ingersoll et al. 2001, Besser et al. 2009a, 2009b, MacDonald et al. 2000, 2009, Allert et al. 2011) is simply the sum of each metal's PEQ. The mean PEQ is the ∑PEQs divided by the number of metals in the mixture, which may normalize the sample (Long et al. 1998, MacDonald et al. 2000, Ingersoll et al. 1998, 2001, 2002, 2009, Besser et al. 2008, 2009b). Although the ∑PEQ and mean PEQs are different methods of measuring effects from a mixture of metals, both methods are used here.

The $\sum PEQ_{Cd, Pb, Zn}$ and mean $PEQ_{Cd, Pb, Zn}$ may then be compared to threshold levels for the mixture or combination of metals. The thresholds for $\sum PEQ_{Cd, Pb, Zn} = 7.92$ and the mean $PEQ_{Cd, Pb, Zn} = 1.11$ (MacDonald et al. 2009). Metals quotients above these threshold levels suggest that the mixture or combination of metals in the fine sediment is likely toxic to the macroinvertebrate community.

2.7 Quality Control

Quality control procedures were consistent with applicable MDNR SOPs and the *SMSBPP* (MDNR 2012). Macroinvertebrate community and water physicochemical variables were duplicated for every 10 stations sampled. Duplicate macroinvertebrate and water quality samples were collected and analyzed at Silver Creek (i.e., 1a and 1b) in the fall of 2012.

3.0 Results

Results for stream habitat assessments, biological assessments that include macroinvertebrate community and water quality analyses, dissolved metals analyses for surface water and pore water, and fine sediment metals character are included in this section. Results are grouped by season. Trends and notable results are highlighted.

3.1 Stream Habitat Assessment

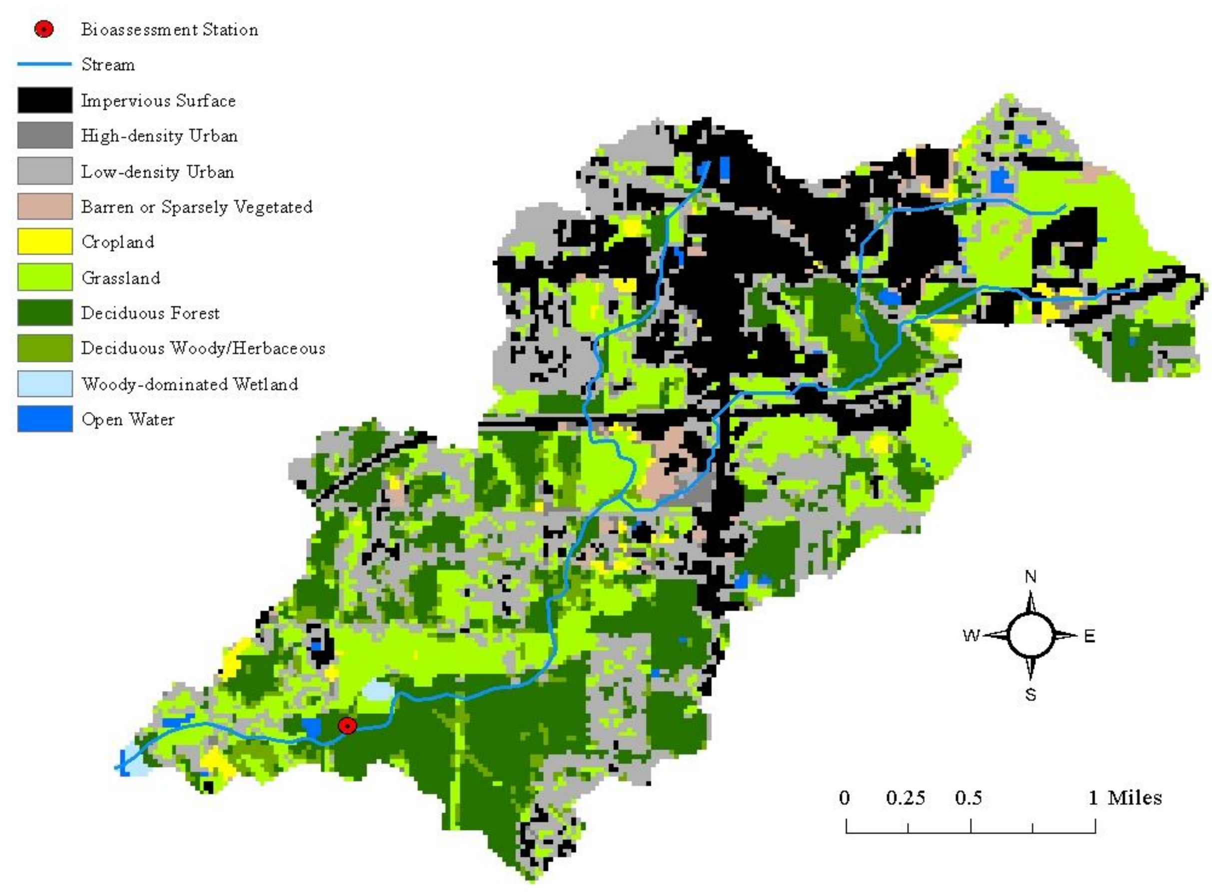
Stream habitat assessment scores were compared between Silver Creek #1 and the mean SHAPP control score (Table 3). Silver Creek #1 exceeded the ≥75 percent similarity threshold with the SHAPP control. Silver Creek #1 had a SHAPP score of 124, which equated to 93 percent of the Mikes Creek #3 (in 2009 and 2013) mean score of 133. Results of this comparison indicate that stream habitat quality at Silver Creek #1 was comparable to the controls and should not negatively influence the results (MNDR 2010a).

The 6.2 square-mile watershed that supports Silver Creek is largely composed of urban land use (Figure 3). Over 45 percent of the watershed upstream from station #1 is made up of impervious surfaces and high-density urban and low-density urban land cover. However, much of the watershed adjacent to Silver Creek #1 consists of deciduous forest and grassland.

Table 3
Stream Habitat Assessment Project Procedure (SHAPP) Scores and Comparisons with SHAPP Control Streams

Station	SHAPP Score	Percent Mean of Controls
Silver Creek #1	124	93
Mikes Creek #3 (2009)	138	mean = 133
Mikes Creek #3 (2013)	127	

Figure 3: Silver Creek #1, Newton County, Watershed Land-Use 2012 – 2013



3.2 Biological Assessment

Biological assessments consist of macroinvertebrate community analyses and general water quality analyses. These are grouped by station and season.

3.2.1 Macroinvertebrate Community Analyses: Primary Metrics

MSCI scores indicated that Silver Creek #1a and #1b (QC duplicates) were partially supporting of the beneficial use for AQL in the fall (Table 4a). Station #1a had an MSCI score of 14 and station #1b had a score of 12. At station #1a, the TR, EPTT, and SDI biological metric values attained scores of 3, while the BI reached the optimum score of 5. At station #1b, the TR and SDI had scores of 3, while the EPTT scored 1. The BI reached a score of 5 in the fall.

The individual metric values that contributed to the less than optimum MSCI in the fall samples were TR, EPTT, and SDI. The TR in #1a and #1b contained 25 and 28 fewer taxa than the optimum BIOREF metric number (>77), respectively. There were 10 fewer EPTT at #1a and 14 fewer EPTT at #1b than the optimum BIOREF metric score (>24). The SDIs were as much as 0.41 less than the optimum BIOREF SDI score (>2.97).

Duplicate samples #1a and #1b had MSCI scores of 14 and 12, respectively, due to slight differences in individual metric scores. Although both samples were found to be partially supporting of the AQL, the slight difference between MSCI scores implies that the investigators were not successful in collecting identical samples. The difference in MSCI scores between #1a and #1b was mainly due to the collection of four fewer EPTT at #1b than #1a, which resulted in an EPTT score of 1 at #1b and 3 at #1a. Despite the slight difference in scores between #1a and #1b, the Quality Similarity Index (**QSI**, MDNR 2012) indicated there was an 82.5 percent similarity between Silver Creek #1a and #1b, which well exceeds the SMSBPP acceptable quality control range.

Table 4a
Biological Criteria Reference (BIOREF) Stream Metric Scores, Individual Metric Values and Scores, Macroinvertebrate Stream Condition Index (MSCI) Scores, and Biological Support Categories for Silver Creek #1a and #1b, Fall 2012

Stream and Station Number	Sample No.	TR	EPTT	BI	SDI	MSCI	Support
Silver Creek #1a	120110	**53$_{(3)}$**	**15$_{(3)}$**	5.0$_{(5)}$	**2.57$_{(3)}$**	**14**	**P**
Silver Creek #1b	120111	**50$_{(3)}$**	**11$_{(1)}$**	4.8$_{(5)}$	**2.71$_{(3)}$**	**12**	**P**
Metric Score=5	↔	>77	>24	<5.5	>2.97	20-16	Full
Metric Score=3	↔	77-39	24-12	5.5-7.7	2.97-1.49	14-10	Partial
Metric Score=1	↔	<39	<12	>7.7	<1.49	8-4	Non

MSCI Scoring Table (bottom) developed from BIOREF streams (n=10); TR=Taxa Richness; EPTT=Ephemeroptera, Plecoptera, Trichoptera Taxa; BI=Biotic Index; SDI=Shannon Diversity Index; (#subscript)=Individual metric score; **Bold**=less than optimum score.

Silver Creek is considerably smaller than many BIOREF streams in the Ozark/Neosho EDU. In order to determine if stream size contributed to the MSCI score at Silver Creek, the metric values were compared to criteria generated using small candidate reference streams of the Ozark/Neosho EDU (MDNR 2011a, Table 4b). The small candidate reference stream criteria were considerably different from the larger BIOREF criteria in the fall, having fewer TR, EPTT, a lower BI, and a higher SDI. Because the small stream criteria were generally lower than BIOREF criteria, and subsequently closer to Silver Creek metric values, it appears that stream size may have had an effect on the macroinvertebrate community composition. However, when Silver Creek #1 metric values were compared to the candidate reference stream criteria, only the Silver Creek EPTT metric score increased from 1 to 3 at #1b. This increased the MSCI from 12 to 14. The slightly higher MSCI score was not sufficient to change the partial support designation for the fall season at Silver Creek #1.

Table 4b
Candidate Reference Stream Biological Criteria, Individual Metric Values and Scores, ΔMacroinvertebrate Stream Condition Index (MSCI) Scores, and ΔBiological Support Categories for Silver Creek #1a and #1b , Fall 2012

Stream and Station Number	Sample No.	TR	EPTT	BI	SDI	ΔMSCI	ΔSupport
Silver Creek #1a	120110	$53_{(3)}$	$15_{(3)}$	$5.0_{(5)}$	$2.57_{(3)}$	14 (NC)	**P** (NC)
Silver Creek #1b	120111	$50_{(3)}$	$11_{(1\rightarrow3)}$	$4.8_{(5)}$	$2.71_{(3)}$	12→14	**P** (NC)
Metric Score=5	↔	>59	>20	<5.30	>3.07	20-16	**F**ull
Metric Score=3	↔	59-29	20-10	5.30-7.70	3.07-1.54	14-10	**P**artial
Metric Score=1	↔	<29	<10	>7.70	<1.54	8-4	**N**on

MSCI Scoring Table (in light gray) developed from small candidate reference stream samples (n=5); TR=Taxa Richness; EPTT=Ephemeroptera, Plecoptera, Trichoptera Taxa; BI=Biotic Index; SDI=Shannon Diversity Index; (#subscript)=Individual metric score; NC=no change.

Silver Creek #1 was partially supporting of the beneficial use for AQL in the spring of 2013 due to suboptimal scores for all metrics (Table 5a). As a result, the MSCI score was 10 at station #1. The TR, BI, and SDI contributed to the MSCI with metric scores of 3, while the EPTT received a metric score of 1. The TR was 14 less than the optimum BIOREF scoring range. Silver Creek #1 had fewer than half the number of EPTT (12) necessary to reach the optimum scoring range (>27) in spring 2013. The BI value was 0.7 higher than the optimum, suggesting that the macroinvertebrate community comprised slightly more tolerant taxa than the BIOREFs. The SDI (2.99) was slightly lower than the optimum range (>3.01). Overall, the Silver Creek community had fewer total taxa, fewer EPTT taxa, was more tolerant to organic pollutant influences, and was less diverse and evenly distributed than BIOREF streams in the EDU.

Table 5a
Biological Criteria Reference (BIOREF) Stream Metric Scores, Individual Metric Values and Scores, Macroinvertebrate Stream Condition Index (MSCI) Scores, and Biological Support Category for Silver Creek #1, Spring 2013

Stream and Station Number	Sample No.	TR	EPTT	BI	SDI	MSCI	Support
Silver Creek #1	131904	**59$_{(3)}$**	**12$_{(1)}$**	**6.0$_{(3)}$**	**2.99$_{(3)}$**	**10**	**P**
Metric Score=5	↔	>72	>27	<5.30	>3.01	20-16	**F**ull
Metric Score=3	↔	72-36	27-13	5.30-7.7	3.01-1.51	14-10	**P**artial
Metric Score=1	↔	<36	<13	>7.7	<1.51	8-4	**N**on

MSCI Scoring Table (bottom) developed from BIOREF streams (n=12); TR=Taxa Richness; EPTT=Ephemeroptera, Plecoptera, Trichoptera Taxa; BI=Biotic Index; SDI=Shannon Diversity Index; (#subscript)=Individual metric score; **Bold**=less than optimum BIOREF score.

Spring Silver Creek metric values were compared to Ozark/Neosho EDU small candidate reference stream criteria to determine if stream size influenced the partial support status (MDNR 2011; Table 5b). Compared to fall, the spring small candidate reference stream criteria were much more similar to the BIOREF criteria, with the exception of the BI and SDI candidate reference threshold values. When Silver Creek #1 metric values were compared to the small stream criteria, only the SDI metric score changed from 3 to 5. In turn, the MSCI score increased from 10 to 12. The slight increase in the MSCI was not sufficient to change the partial support category designation. Therefore, it appears that stream size was again not a major contributor to the MSCI score.

Table 5b
Candidate Reference Stream Biological Criteria, Individual Metric Values and Scores, ΔMacroinvertebrate Stream Condition Index (MSCI), and ΔBiological Support Category for Silver Creek #1, Spring 2013

Stream and Station Number	Sample No.	TR	EPTT	BI	SDI	ΔMSCI	ΔSupport
Silver Creek #1	131904	59$_{(3)}$	12$_{(1)}$	6.0$_{(3)}$	2.99$_{(3\rightarrow5)}$	10→12	**P (NC)**
Metric Score=5	↔	>71	>26	<4.60	>2.92	20-16	**F**ull
Metric Score=3	↔	71-35	26-13	4.60-7.30	2.92-1.49	14-10	**P**artial
Metric Score=1	↔	<35	<13	>7.30	<1.49	8-4	**N**on

MSCI Scoring Table (in light gray) developed from small candidate reference stream samples (n=6); TR=taxa richness; EPTT=Ephemeroptera, Plecoptera, Trichoptera Taxa; BI=Biotic Index; SDI=Shannon Diversity Index; (#subscript)=Individual metric score; NC=no change.

3.2.2 Dominant Macroinvertebrate Taxa

The 10 most DMT found in BIOREF streams of the EDU were compared with the fall Silver Creek #1 taxa list (Table 6). Four of the top 10 most abundant taxa in the BIOREF streams were not found in Silver Creek #1. *Cheumatopsyche*, *Marilia*, *Lirceus*, and *Optioservus sandersoni* were among the top 10 taxa in the BIOREF streams, but they were not present in the Silver Creek samples. The mayfly *Caenis latipennis* was also among the BIOREF DMT in the fall, but it was absent from the Silver Creek #1b (duplicate) and found as a much lower percentage of the total sample in Silver Creek #1a.

Table 6
DMT Percentage (and Rank) per Taxon for BIOREF and
Silver Creek #1a and #1b, Fall 2012

Dominant Taxa	BIOREF	Silver Creek #1a	Silver Creek #1b
Psephenus herricki	15.94 (1)	28.15 (1)	23.70 (1)
Hyalella azteca	8.22 (2)	11.19 (3)	7.00 (4)
Cheumatopsyche	4.83 (3)	0.00	0.00
Paraleptophlebia	4.63 (4)	**Leptophlebiidae* 13.51 (2)	**Leptophlebiidae* 17.59 (2)
Baetis	3.16 (5)	4.80 (5)	5.07 (6)
Marilia	3.15 (6)	0.00	0.00
Caenis latipennis	3.13 (7)	0.15 (26)	0.00
Lirceus	3.11 (8)	0.00	0.00
Stenelmis	3.07 (9)	1.80 (13)	6.18 (5)
Optioservus sandersoni	2.85 (10)	0.00	0.00

*Specimens in the fall were identified only to family level due to the small size. Although these were probably small *Paraleptophlebia*, a definite genus level diagnosis could not be made.

The 10 most DMT found in BIOREF streams of the Ozark/Neosho EDU were compared with the spring Silver Creek taxa list (Table 7). Eight of the BIOREF DMT either were not found in Silver Creek or the percentage was considerably lower in Silver Creek. Six of the dominant taxa from BIOREF streams, which include *Leucrocuta*, *Paraleptophlebia*, *Elimia*, *Eurylophella bicolor*, *Acentrella*, and *Optioservus sandersoni*, were not found in Silver Creek #1. *Lirceus* and *Thienemannimyia* grp. were much less abundant as a percentage of the total number of individuals in the Silver Creek spring sample.

Table 7
DMT Percentage (and Rank) per Taxon for BIOREF and Silver Creek #1, Spring 2013

Dominant Taxa	BIOREF	Silver Creek #1
Lirceus	13.13 (1)	0.34 (29)
Cricotopus/Orthocladius	10.64 (2)	13.52 (3)
Leucrocuta	3.86 (3)	0.00
Paraleptophlebia	3.62 (4)	0.00
Thienemannimyia grp.	3.39 (5)	1.09 (16)
Elimia	3.17 (6)	0.00
Eurylophella bicolor	2.77 (7)	0.00
Acentrella	2.73 (8)	0.00
Diphetor	2.55 (9)	15.37 (1)
Optioservus sandersoni	2.14 (10)	0.00

3.2.3 General Water Quality Analyses

None of the water quality parameters analyzed in fall 2012 or spring 2013 were outside WQSs (MDNR 2014; Table 8). Flow was approximately five times higher in the spring than fall. Turbidity (5.03 NTU) was higher in the spring and exceeded EPA (2000) suggested guidelines (2.3 NTU). Nutrients, such as TN at #1a (0.64 mg/L) and #1b (0.62 mg/L), along with nitrate + nitrite as nitrogen at #1a (0.55 mg/L) and #1b (0.56 mg/L) were present in concentrations that exceeded EPA suggested guidelines (0.093 mg/L) in the fall. In the spring sample, Silver Creek #1, the TN (1.44 mg/L) and nitrate+nitrite as nitrogen concentrations (1.27 mg/L) both exceeded the EPA suggested thresholds of 0.31 mg/L and 0.093 mg/L, respectively. The chloride concentration in the spring (42 mg/L) was nearly twice that of the fall (25 mg/L) sample.

3.3 Dissolved Metals

Dissolved metals concentrations in surface water and pore water were examined. Surface water was collected in the fall and spring via grab samples, whereas pore water samples were collected using passive sampling devices (peepers, Brumbaugh et al. 2007) during a 14-day deployment period in August.

Table 8
Physicochemical Water Parameters for Silver Creek #1a and #1b in Fall 2012 and Station #1 in Spring 2013

Station/Date Parameter	Silver Creek #1a Fall 10-4-12	Silver Creek #1b Fall 10-4-12	Silver Creek #1 Spring 4-2-13
Sample Number	1204449	1204450	131712
pH (Units)	7.9	--	7.8
Temperature (°C)	15.0	--	9.0
Conductivity (µS/cm)	430	--	471
Dissolved O_2	8.57	--	11.58
Discharge (cfs)	0.12	--	5.28
NFR	<5	<5	$<5_{03}$
Turbidity (NTUs)	0.85	1.25	**5.03**
TN	**0.64**	**0.62**	**1.44**
Nitrate+Nitrite as N	**0.55**	**0.56**$_{06}$	**1.27**
Ammonia-N	<0.03	<0.03	0.050
Sulfate	16.0	15.9	21.1
Chloride	25.5	25.7	42.4
Total Phosphorus	$<0.01_{08}$	$<0.01_{08}$	<0.01

Units mg/L unless otherwise labeled; **Bold**=Exceed EPA (2000) suggested criteria. Qualifiers - $\#_{03}$=exceeded holding time; $\#_{06}$=estimated value, QC data outside limits; $\#_{08}$=analyte present in blank at ½ reported value.

3.3.1 Surface Water Metals

Surface water grab samples from Silver Creek #1 contained several dissolved metals in the fall and spring (Table 9). Barium, copper, nickel, and zinc were detected in low levels in the surface water grab samples collected in the fall and spring. Metals concentrations were relatively similar between duplicate samples in the fall. However, copper concentrations were slightly different between duplicates #1b (0.5 µg/L estimated value, below PQL) and #1a (<0.5 µg/L). The spring zinc surface water concentration (13.9 µg/L) was nearly two times higher than the fall duplicate samples (#1a 7.7 µg/L and #1b 7.86 µg/L). None of the dissolved metals exceeded WQSs (MDNR 2014) during either season.

3.3.2 Pore Water Metals

Several dissolved metals were detected in the pore water samples collected in August 2013 (Table 10). Dissolved barium, cobalt, copper, iron, manganese, and nickel were detected in peeper samples from pool habitat (NF). All were found in low concentrations, except for iron and manganese. Iron and manganese exceeded WQSs (MDNR 2014) at two pool locations. Iron exceeded WQSs for the AQL (1000µg/L) in one pool (1074 µg/L at NF2). Manganese exceeded WQSs for the beneficial use for the protection of groundwater (50 µg/L) in one pool at two locations (322 µg/L at NF2 and 3280 µg/L at NF3).

Table 9
Surface Water (Grab sample) Dissolved Metals (µg/L) and Hardness (as $CaCO_3$) for Silver Creek #1a and #1b in Fall 2012 and Silver Creek #1 in Spring 2013

		Parameter									
Station	Sample Number	Ba	Cd	Co	Cu	Pb	Ni	Zn	Ca (mg/L)	Mg (mg/L)	HARD $CaCO_3$
Silver Creek #1a, Fall 2012	1204449	87.9	<0.1	<1	<0.5	<0.5	2.35	7.77	74.8	3.66	202
Silver Creek #1b, Fall 2012	1204450	87.5	<0.1	<1	0.5_{05}	<0.5	2.35	7.86	75.1	3.63	202
Silver Creek #1, Spring 2013	131712	89.0	<0.10	<1	0.74_{05}	<0.50	2.06	13.9	65.0	3.74	178

Units µg/L unless otherwise labeled; Sample numbers are the same as those in the physicochemical water parameters table.
Qualifiers - $\#_{05}$=estimated value, detected below PQL

Table 10
Pore Water (Peeper samples) Dissolved Metals (µg/L; Ca and Mg=mg/L) and Hardness (mg/L as $CaCO_3$) for Silver Creek, August 1-14, 2013

		Parameter											
Station, Habitat-replicate	Sample Number	Ba	Cd	Ca	Co	Cu	Fe	Pb	Mg	Mn	Ni	Zn	HARD $CaCO_3$
Silver Creek, CS1	133724	97.6	<0.10	69.6	<1	<0.5	<1	<0.50	3.58	<0.50	1.10_{05}	N/A	189
Silver Creek CS2	133725	95.0	<0.10	72.2	<1	<0.5	2.06_{05}	<0.50	3.74	<0.50	1.08_{05}	N/A	196
Silver Creek, CS3	133726	96.6	<0.10	73.0	<1	1.04_{05}	2.38_{05}	<0.50	<0.10	<0.50	1.08_{05}	N/A	198
Silver Creek, NF1	N/A	--	--	--	--	--	--	--	--	--	--	--	--
Silver Creek, NF2	133727	140.2	<0.10	60.0	<1	<0.5	2.38_{05}	<0.50	2.98	**322**	1.20_{05}	N/A	162
Silver Creek, NF3	133728	204	<0.10	64.8	5.10_{05}	<0.5	**1074**	<0.50	3.12	**3280**	2.10_{05}	N/A	175
MEAN	--	126.68	--	67.9	--	--	207.21	--	3.36	1801	1.31	N/A	184
S.D. n-1	--	47.21	--	5.46	--	--	464.07	--	0.36	2092	0.44	N/A	15
WQS for AQL (MDNR 2014)	--	--	0.04	--	500 LWW*	15	1000 AQL*	5	--	50 GW*	87.1	197	@184
Field Blank 1	133720	<0.50	<0.10	<0.10	<1	<0.50	<1	<0.50	<0.10	<0.50	<0.50	**48.4**	<0.66
Field Blank 2	133721	<0.50	<0.10	<0.10	<1	<0.50	<1	<0.50	<0.10	<0.50	<0.50	**40.4**	<0.66
Field Blank 3	133722	<0.50	<0.10	<0.10	<1	<0.50	<1	<0.50	<0.10	<0.50	<0.50	**49.0**	<0.66
Bottle Blank	133723	<0.50	<0.10	<0.10	<1	<0.50	<1	<0.50	<0.10	<0.50	<0.50	<0.50	<0.66

Units µg/L unless otherwise labeled; **Bold**=notable, outside WQS acceptable range or trend; N/A=not available; *=not hardness dependent WQS and beneficial use; CS=riffle, NF=pool; Qualifiers - $\#_{05}$=estimated value, detected below PQL.

Peeper blanks were utilized to address quality assurance and quality control. Three field blanks were used to identify potential contamination during deployment, deployment period, and retrieval, while one bottle blank was used to identify contaminants associated with the peeper components. The bottle blank contained no dissolved metals, while all three field blanks contained dissolved zinc (Table 10). Due to the apparent zinc contamination in the field blanks, the dissolved zinc results using peepers were not considered valid, and they were removed from consideration.

3.4 Fine Sediment Character

Fine sediment samples from Silver Creek #1 were characterized for cadmium, lead, and zinc concentrations (Table 11). Total recoverable metals results were compared to individual metals and mixture of metals thresholds. PEC (PEC; MacDonald et al. 2000) and Probable Effects Quotients (PEQ, Besser et al. 2009a, MacDonald et al. 2000) were compared to individual metals concentrations in Silver Creek. Cadmium concentrations did not exceed the PEC in either season. The lead concentration in the fine sediment sample (157 mg/kg) exceeded the PEC (128 mg/kg) in the fall. Subsequently, the PEQ (1.226) also exceeded the suggested threshold PEQ (>1.0). The fall zinc concentration (454 mg/kg) was only slightly lower than the PEC (459 mg/kg), and the PEQ (0.989) was slightly below the recommended PEQ threshold (>1.0). To account for a mixture of cadmium, lead, and zinc, the $\sum PEQ_{Cd,\ Pb,\ Zn}$ and mean $PEQ_{Cd,\ Pb,\ Zn}$ were compared to their respective quotient thresholds. The mixture or combination of fine sediment cadmium, lead, and zinc did not exceed the $\sum PEQ_{Cd,\ Pb,\ Zn}$ or the mean $PEQ_{Cd,\ Pb,\ Zn}$ thresholds in either season at Silver Creek #1.

Table 11
Total Recoverable Metals Character in the Fine Sediment (<2.0mm): Cadmium, Lead, and Zinc Concentrations (mg/kg Dry Weight)

Station	Parameter					
	Sample Number	Cadmium	Lead	Zinc	$\sum PEQ_{Cd\ Pb,\ Zn}$	Mean $PEQ_{Cd,\ Pb,\ Zn}$
Silver Creek (fall; mg/kg)	1204437	1.760	**157**	454	--	--
Silver Creek (spring; mg/kg)	131717	1.250	94.5	319	--	--
PEC	**--**	**4.98**	**128**	**459**	--	--
PEQ fall	--	0.353	**1.226**	0.989	2.568	0.856
PEQ spring	--	0.251	0.738	0.695	1.684	0.561
Toxicity Threshold	--	>1.0	>1.0	>1.0	≥7.92	≥1.11

PEC=Probable Effects Concentration (MacDonald et al. 2000); **Bold**=above PEC; PEQ=Probable Effects Quotient, metal value/PEC; Mean PEQ=∑PEQ/#metals; ∑PEQ=sum PEQs.

4.0 Discussion

Results from the Silver Creek (fall 2012 and spring 2013) stream habitat assessment, macroinvertebrate community analyses, general water quality, surface water metals analyses, pore water metals analyses, and fine sediment metals characterizations are included in the discussion.

4.1 Stream Habitat Assessment

The stream habitat score for Silver Creek #1 was compared to the mean of SHAPP controls. The SHAPP score exceeded the 75 percent similarity threshold outlined in the SHAPP (MDNR 2010a). Therefore, Silver Creek #1 should be capable of supporting a reference-quality macroinvertebrate community. High density urban areas and a high percentage of impervious surfaces in the watershed pose potential threats to the habitat quality at Silver Creek #1. However, the stream habitat quality within Silver Creek #1 does not appear to be a contributor to the following results.

4.2 Macroinvertebrate Community

Silver Creek #1 was partially supporting of the beneficial use for the protection of AQL during the fall and spring sample seasons. The fall individual biological metric (i.e., TR, EPTT, BI, and SDI) scores illustrated that Silver Creek had lower TR, fewer EPT taxa, and less diversity than BIOREF streams while the optimal BI score indicated that the macroinvertebrate community comprised taxa that were more sensitive to organic/nutrient enrichment or disturbance. In the spring, all four individual metric scores were sub-optimal, which illustrated that the Silver Creek community had a lower TR, fewer EPTT, was more tolerant to organic pollutants, and was less diverse than the BIOREF streams of the EDU. Generally, these results identify an impaired macroinvertebrate community that may be, in part, intermittently influenced by organic input or disturbance.

To assess if stream size had an effect on the beneficial use support category, Silver Creek metric values were compared to small candidate reference stream criteria from the Ozark/Neosho EDU. In the fall, the candidate reference stream criteria were substantially different from the larger BIOREF criteria; this suggested that the small streams contained fewer TR, EPTT, more sensitive taxa, and sometimes less diverse macroinvertebrate communities than the larger BIOREF streams. The change in criteria resulted in the Silver Creek metric values being slightly closer to attaining higher metric scores. This suggested that stream size may have had some effect on the community composition in the fall. However, when Silver Creek metric values were given metric scores, only the EPTT score increased at station #1b. Subsequently, the MSCI score increased from 12 to 14. Despite the slight change in MSCI score, Silver Creek #1 retained its partial support designation. The smaller size of Silver Creek did not have a substantial influence on the partial support status in the fall.

Unlike in the fall, the spring small candidate reference stream criteria were more similar to the BIOREF criteria, which suggested that small stream macroinvertebrate communities were similar to larger stream communities. The candidate reference BI metric scoring range was slightly lower, which indicated that the taxa in the smaller streams were slightly more sensitive to organic/nutrient influences or disturbance. Also, the small candidate reference SDI metric scoring range was lower, which suggested that smaller streams are less diverse and evenly distributed than larger BIOREF streams. When these small candidate reference stream criteria were compared to Silver Creek metric values, only the SDI metric score increased from 3 to 5. Subsequently, the MSCI increased from 10 to 12. Despite the slight increase in the MSCI score, the partial support designation did not change. Therefore, it appears that stream size was not a substantial contributor to the partial support status of Silver Creek in the spring.

The DMT comparisons illustrated dissimilarities in community composition between the Silver Creek and BIOREF streams of the EDU. Fifty percent of the fall assemblage and 80 percent of the spring Silver Creek taxa were either absent or noticeably reduced when DMT were compared with BIOREF DMT. Clearly, the Silver Creek macroinvertebrate community assemblage was different from the BIOREF communities, based on the abundance or absence of DMT. The DMT illustrate how the macroinvertebrate communities at BIOREF streams differ from Silver Creek, as the stream was dominated by substantially different taxa.

Silver Creek #1 was partially supporting of the beneficial use designation during both seasons. Stream size was not a substantial contributor to the support status, and differences in community composition illustrated that intermittent organic/nutrient input or disturbance may have affected the community composition; however the community was consistently influenced during this study. An additional biological assessment that includes more stations may identify potential sources for the impairment, as well as its extent.

4.2 General Water Quality

All of the general water quality parameters analyzed from both seasons were within MDNR WQSs (MDNR 2014). However, turbidity and some nutrients (TN, NO_3+NO_2-N) were notable in samples from each season. Because there are currently no criteria for turbidity or nutrients in the Missouri WQS (MDNR 2014), turbidity and nutrient results were compared to the EPA December 2000 *Ambient Water Quality Criteria Recommendations for Rivers and Streams in Nutrient Ecoregion XI* (EPA 2000). Turbidity exceeded those suggested thresholds in the spring, probably due to increased flow and subsequent runoff. Nutrient values exceeded these recommendations during the fall and spring. Increased chloride concentrations in the spring may be a result of winter road salt runoff, or along with elevated nutrient concentrations and higher BI, may indicate an upstream organic pollutant source. Urban influences may have contributed these constituents.

4.3 Dissolved Metals

Dissolved metals concentrations were identified using surface water and pore water samples. Surface water was collected in the fall and spring via grab samples, and pore water samples were collected during a 14-day deployment period in August using passive sampling devices (peepers, Brumbaugh et al. 2007).

4.3.1 Surface Water Metals

Several dissolved metals were detected in the fall and spring surface water samples. Copper was detected in one of the duplicates, but as an estimate because it was detected below the PQL. The difference between duplicates was probably due to that estimation. Zinc was nearly two times higher in the spring surface water samples compared to the fall. The higher zinc concentration in the spring may have been related to runoff and subsequent increased flow that was recorded in the spring. None of the dissolved metals exceeded WQSs during either season.

4.3.2 Pore Water Metals

Pore water metals concentrations were relatively similar to surface water results with a few exceptions. Copper was detected (estimated value, detected below PQL) in one of the riffle

samples. Iron and manganese were also found in two pool samples in concentrations that exceeded WQSs (MDNR 2014).

Dissolved iron and manganese concentrations exceeded WQSs (MDNR 2014) in the pore water of Silver Creek pool habitat. The presence of elevated Fe and Mn for a particular peeper indicates that it sampled anoxic pore water, and probably reduced sulfides in the sediment zone where it resided (William Brumbaugh pers. comm. 2013). The presence of sulfides in sediments is often associated with anoxic conditions and elevated Fe in the pore water. Sulfides tend to make Zn less soluble in the pore water. The variation of Fe and Mn among replicate peepers indicates local heterogeneity in sediment substrate (probably sulfides and organic matter, but also greater amounts of fine particles relative to coarse sand or cobble), or that the peepers were placed at inconsistent depths. Those peepers placed deeper and with minimal disturbance would tend to have greater Fe (William Brumbaugh pers. comm. 2013). That being said, the elevated Fe and Mn results that were observed from the two pool samples may be a function of where the peepers were deployed and may not represent aerobic surface or pore water conditions. Alternatively, mobilization of heavy metals in association with the reductive dissolution of Fe and Mn oxides under anaerobic conditions may account for potentially toxic levels of metals in the surface water or bioaccumulation in stream food webs (Brumbaugh et al. 2007, Besser et al. 2009a). Further heavy metals studies should include additional pore water sampling or bioaccumulation analyses.

Because dissolved zinc was detected in all three peeper field blanks, zinc results were not considered valid and were not presented in this report. Recent developments in manufacturing and handling of the peepers have reduced the number of residual metals that have been detected in the field blanks (William Brumbaugh pers. comm. 2013). However, zinc has proven difficult to eliminate from the field blanks. Bottle blanks were prepared in the laboratory (at USGS, CERC) and analyses were conducted within one day; they did not contain any of the tested dissolved metals. This suggests that the peeper components (i.e., filter, bottle, and 1% nitric acid dilutant) did not influence the sample results in the short-term. Conversely, the field blanks were held for the entire deployment period in a container and in a refrigerator before being analyzed with the test samples after retrieval. Dissolved zinc concentrated in the field blank peeper over the deployment period. Alternative methods of manufacturing and handling peeper field blanks may eliminate zinc contamination from future samples. With that in mind, peepers should prove to be an important device for sampling dissolved metals in pore water of streams. As newer models of peepers and methods of handling are developed, peepers should again be used in Silver Creek to identify dissolved metals concentrations in pore water.

4.4 Fine Sediment Character

Individual metals threshold levels (PEC, MacDonald et al. 2000; PEQ, Besser et al. 2009a) and mixture of metals thresholds (∑PEQ and mean PEQ, MacDonald et al. 2000, 2009) were compared to Silver Creek #1 fine sediment total metals concentrations.

Fine sediment metals concentrations or character (i.e., cadmium, lead, and zinc) were examined for individual as well as the combined effects. In the fall, the lead concentration was above the threshold PEC and the recommended PEQ threshold. The total zinc concentration nearly reached the threshold PEC and PEQ in the fall sample. Lead and zinc concentrations were

present in the spring sample as well, but they did not exceed the PEC or PEQ threshold. The combination or mixture of cadmium, lead, and zinc also did not exceed threshold levels.

Results varied by season, which suggests that the metals were not evenly distributed in the Silver Creek #1 substrate. Fine sediment was not necessarily collected from the same locations during both seasons. Since concentrations varied by season, and sample locations were possibly different, fine sediment metals were probably not evenly distributed in the substrate.

Individual metals concentrations in fine sediments may have negatively influenced the macroinvertebrate assemblage at Silver Creek #1. Besser et al. (2009a) found that metals in fine sediment contributed to adverse ecological effects in streams draining the Viburnum Trend mining district. TR and EPTT are the best biological indicators of metals effects in streams (Soucek et al. 2000; Clements et al. 2000). TR and EPTT in Silver Creek were much lower than their respective optimum BIOREF or candidate reference scoring thresholds during both seasons. Furthermore, mayflies and stoneflies are among the most sensitive macroinvertebrate groups to heavy metals contamination in streams (Ryck 1974; Burrows and Whitton 1983; Kiffney and Clements 1994; Carlisle and Clements 1999; Yuan and Norton 2003; Poulton et al. 2009), and their tolerance may be pH dependent (Feldmann and Connor 1992; Yuan and Norton 2003; Poulton et al. 2009). These trends are consistent with this study. Eleven mayfly taxa were found in the fall in Silver Creek, while BIOREF streams had a combined total of 25 taxa. Seven mayfly taxa were collected in the spring, while the spring BIOREF streams contained a combined total of 26 taxa. Similarly, stoneflies were absent from both fall samples and the spring Silver Creek sample, while BIOREF streams contained combined totals of seven stonefly taxa in the fall and 13 in the spring. This study suggests that heavy metals may be contributing to the partial support status of the AQL beneficial use category at these stations. Additional fine sediment characterizations should be conducted in other areas of Silver Creek.

5.0 Conclusions

The objectives have been met. The stream habitat, macroinvertebrate community, physicochemical water quality, and dissolved metals concentrations in the surface water and pore water have been assessed. Fine sediment metals character in the substrate has been identified.

Testing the null hypotheses resulted in the following:

1) Stream habitat quality at Silver Creek #1 was comparable to the SHAPP control stream (Mikes Creek #3).

2) MSCI scores illustrated that Silver Creek #1 was partially supporting of the beneficial use for the protection of AQL during both seasons. In the fall, the TR, EPTT, and SDI contributed to the suboptimal score, with the BI being the only biological metric in the optimum range. However, all of the individual metrics contributed to the low spring MSCI score, which suggests that a potentially intermittent organic/nutrient influence or disturbance may contribute to its status.

3) Comparisons of the small candidate reference criteria illustrated that Silver Creek was not substantially affected by stream size. MSCI scores increased slightly, but the support category did not change. This indicated that stream size was not a substantial contributor to the status of the stream. In the fall, the candidate reference criteria and the BIOREF criteria were very different, suggesting that stream size potentially had an effect on metric scores by lowering the criteria threshold values. Silver Creek values were closer to several of the optimum levels. In the spring, the candidate reference criteria were very similar to the BIOREF criteria, suggesting that stream size had little influence on Silver Creek criteria thresholds. Despite the lowering of several criteria thresholds and subsequent slight increases in the MSCIs, Silver Creek #1 remained partially supporting of the AQL during both seasons.

4) Physicochemical water quality variables were within acceptable MDNR WQSs (2014). However, the nutrients TN and nitrate+nitrite as nitrogen exceeded EPA (2000) suggested guidelines during both seasons and turbidity exceeded EPA guidelines in the spring. Elevated nutrient levels may be due to urban or mine related influences.

5) Dissolved metals concentrations were similar between surface water and pore water with the two exceptions. Iron and manganese were detected above WQSs in peeper pore water samples collected in pools. Anoxic conditions in pool sediment are likely to have contributed to these readings; however, they may also identify potential heavy metals influences.

6) The metals character in the fall sediment sample included total lead concentrations that exceeded the lead PEC and PEQ thresholds, as well as total zinc that was near the zinc PEC threshold. The combination or mixture of these metals did not exceed the $\sum PEQ_{Cd, Pb, Zn}$ or mean $PEQ_{Cd, Pb, Zn}$ thresholds. Metals concentrations in the fine sediment varied between seasons, which suggested that fine sediment containing metals was not evenly distributed within Silver Creek.

6.0 Recommendations

1) Consider conducting an additional bioassessment and fine sediment characterization study that includes other areas of Silver Creek.

2) Work toward the development of a heavy metals BI for macroinvertebrates.

3) Newer model peepers and other long-term sample devices (e.g., Diffusive Gradients in Thin-film [DGT] and Stabilized Liquid Membrane Device [SLMD] in development by the USGS CERC laboratory) should be deployed in Silver Creek and other mine-related streams to identify heavy metals concentrations in pore water.

7.0 Literature Cited

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Appendix A

Macroinvertebrate Database Bench Sheets Report for Silver Creek, Newton County, Grouped by Season

Aquid Invertebrate Database Bench Sheet Report

Silver Cr [120110], Station #1a, Sample Date: 10/4/2012 11:00:00 AM

CS = Coarse; NF = Nonflow; RM = Rootmat; -99 = Presence

ORDER: TAXA	CS	NF	RM
AMPHIPODA			
Hyalella azteca		5	144
Stygobromus	1		
ARHYNCHOBDELLIDA			
Erpobdellidae		-99	-99
BASOMMATOPHORA			
Ancylidae		4	
Gyraulus			1
Menetus			38
COLEOPTERA			
Dubiraphia		1	29
Neoporus			2
Psephenus herricki	329	45	1
Stenelmis	12	3	9
DECAPODA			
Orconectes neglectus	1	-99	-99
DIPTERA			
Ablabesmyia			1
Ceratopogoninae	1	2	
Chironomus		1	
Corynoneura		1	
Cricotopus/Orthocladius	2	1	
Dicrotendipes		1	3
Microtendipes		20	3
Nanocladius			1
Paraphaenocladius			1
Paratanytarsus			5
Paratendipes		7	1
Polypedilum convictum	1		
Polypedilum illinoense grp	1		1
Stenochironomus			1
Tanytarsus			1
Thienemannimyia grp.			1
EPHEMEROPTERA			
Acentrella	2		
Acerpenna	1		
Baetis	64		
Caenis latipennis		2	
Diphetor	26		1
Fallceon			1
Leptophlebiidae	27	137	16

Aquid Invertebrate Database Bench Sheet Report

Silver Cr [120110], Station #1a, Sample Date: 10/4/2012 11:00:00 AM

CS = Coarse; NF = Nonflow; RM = Rootmat; -99 = Presence

ORDER: TAXA	CS	NF	RM
Maccaffertium pulchellum	47		
Procloeon		1	1
Stenacron	23	37	1
Stenonema femoratum	37	108	2
HEMIPTERA			
Mesovelia			1
LEPIDOPTERA			
Petrophila	1		1
LUMBRICINA			
Lumbricina	4	-99	-99
LUMBRICULIDA			
Lumbriculidae	4	2	1
ODONATA			
Argia	16	9	4
Boyeria			-99
Calopteryx			1
Gomphidae	7	1	
TRICHOPTERA			
Chimarra	2		
Oecetis		1	1
Polycentropus	5		2
Triaenodes			4
TRICLADIDA			
Planariidae	23		3
TUBIFICIDA			
Tubificidae		11	
VENEROIDA			
Pisidiidae	1	9	2

Aquid Invertebrate Database Bench Sheet Report

Silver Cr [120111], Station #1b, Sample Date: 10/4/2012 11:00:00 AM

CS = Coarse; NF = Nonflow; RM = Rootmat; -99 = Presence

ORDER: TAXA	CS	NF	RM
"HYDRACARINA"			
Acarina	1	1	
AMPHIPODA			
Hyalella azteca			94
ARHYNCHOBDELLIDA			
Erpobdellidae	1	1	
BASOMMATOPHORA			
Ancylidae		3	5
Menetus	2		19
COLEOPTERA			
Dubiraphia	1	3	30
Ectopria nervosa		1	
Psephenus herricki	248	69	1
Stenelmis	44	15	24
DECAPODA			
Orconectes neglectus	3		1
DIPTERA			
Ablabesmyia		6	
Brillia			1
Ceratopogoninae		1	
Chironomidae			1
Corynoneura			1
Cricotopus/Orthocladius	1	2	1
Cryptochironomus		1	
Labrundinia			1
Microtendipes		5	1
Paratanytarsus	1	1	4
Paratendipes		3	8
Polypedilum convictum	1		
Polypedilum illinoense grp	1		
Polypedilum scalaenum grp	1		
Stempellinella		1	
Stenochironomus	1		
Tanytarsus			1
Thienemannimyia grp.	1		
Zavrelimyia	1		
EPHEMEROPTERA			
Acentrella	3		
Baetis	68		
Diphetor	26		
Leptophlebiidae	49	150	37

Aquid Invertebrate Database Bench Sheet Report

Silver Cr [120111], Station #1b, Sample Date: 10/4/2012 11:00:00 AM

CS = Coarse; NF = Nonflow; RM = Rootmat; -99 = Presence

ORDER: TAXA	CS	NF	RM
Maccaffertium pulchellum	48		
Procloeon	2		2
Stenacron	30	21	2
Stenonema femoratum	34	70	3
HEMIPTERA			
Rhagovelia	2		
LEPIDOPTERA			
Petrophila	1		
LUMBRICINA			
Lumbricina	11	-99	1
LUMBRICULIDA			
Lumbriculidae	3	6	
ODONATA			
Argia	12	9	4
Calopteryx			2
Gomphidae	1		
TRICHOPTERA			
Chimarra	8		
Polycentropus	9	5	1
Triaenodes			6
TRICLADIDA			
Planariidae	43		5
TUBIFICIDA			
Tubificidae		18	3
VENEROIDA			
Pisidiidae		10	23

Aquid Invertebrate Database Bench Sheet Report

Silver Cr [131904], Station #1, Sample Date: 4/2/2013 12:15:00 PM

CS = Coarse; NF = Nonflow; RM = Rootmat; -99 = Presence

ORDER: TAXA	CS	NF	RM
"HYDRACARINA"			
Acarina	2	4	
AMPHIPODA			
Hyalella azteca			17
ARHYNCHOBDELLIDA			
Erpobdellidae		-99	
BASOMMATOPHORA			
Ancylidae		2	1
Menetus			3
COLEOPTERA			
Berosus	1		
Dubiraphia		1	9
Psephenus herricki	38	15	-99
Stenelmis	12	4	9
DECAPODA			
Orconectes neglectus	-99	1	-99
DIPTERA			
Ablabesmyia		19	11
Ceratopogoninae		2	3
Clinocera	9		
Corynoneura			1
Cricotopus bicinctus			1
Cricotopus/Orthocladius	66	28	67
Cryptochironomus		1	
Diamesa	1		
Dicrotendipes		6	5
Hydrobaenus			1
Microtendipes		4	
Nanocladius	2		4
Nilotanypus	1		
Paraphaenocladius	1		1
Paratanytarsus			6
Paratendipes	1	13	4
Polypedilum convictum	29		5
Polypedilum halterale grp	1		
Polypedilum illinoense grp			2
Polypedilum scalaenum grp		1	
Rheocricotopus	23	1	7
Rheotanytarsus	1	1	1
Synorthocladius		1	
Tanytarsus	1	2	5

Aquid Invertebrate Database Bench Sheet Report

Silver Cr [131904], Station #1, Sample Date: 4/2/2013 12:15:00 PM

CS = Coarse; NF = Nonflow; RM = Rootmat; -99 = Presence

ORDER: TAXA	CS	NF	RM
Thienemanniella		1	
Thienemannimyia grp.	3		10
Tipula	-99		
Zavrelimyia	1	2	1
EPHEMEROPTERA			
Caenis latipennis			1
Diphetor	157	2	24
Fallceon	34		30
Leptophlebia	1	13	54
Maccaffertium pulchellum	24		2
Stenacron	17	30	4
Stenonema femoratum	32	121	11
ISOPODA			
Lirceus	1	1	2
LUMBRICULIDA			
Lumbriculidae	2	5	1
ODONATA			
Argia		4	1
Calopteryx			1
Gomphidae	5		
TRICHOPTERA			
Chimarra	64		
Ironoquia	1		-99
Oecetis			1
Polycentropus	1	4	1
Triaenodes			1
TRICLADIDA			
Planariidae	31	8	6
TUBIFICIDA			
Limnodrilus hoffmeisteri		1	
Tubificidae		1	2
VENEROIDA			
Pisidiidae		4	9